

A thermodynamic theory of solid viscoelasticity. Part I: Linear viscoelasticity

A. D. Freed

*NASA Glenn Research Center, Polymers Branch, MS 49-3, 210000 Brookpark Road, Brook Park, Ohio
44135, USA*

A. I. Leonov¹

The University of Akron, Department of Polymer Engineering, Akron, Ohio 44325-0301, USA

Abstract

The present series of three consecutive papers develops a general theory for linear and finite solid viscoelasticity. Because the most important object for nonlinear studies are rubber-like materials, the general approach is specified in a form convenient for solving problems important for many industries that involve rubber-like materials. General linear and nonlinear theories for non-isothermal deformations of viscoelastic solids are developed based on the quasi-linear approach of non-equilibrium thermodynamics.

In this, the first paper of the series, we analyze non-isothermal linear viscoelasticity, which is applicable in a range of small strains not only to all synthetic polymers and bio-polymers but also to some non-polymeric materials. Although the linear case seems to be well developed, there still are some reasons to implement a thermodynamic derivation of constitutive equations for solid-like, non-isothermal, linear viscoelasticity. The most important is the thermodynamic modeling of “thermo-rheological complexity”, i.e. different temperature dependences of relaxation parameters in various parts of relaxation spectrum. A special structure of interaction matrices is established for different physical mechanisms contributed to the normal relaxation modes. This structure seems to be in accord with observations, and creates a simple mathematical framework for both continuum and molecular theories of the thermo-rheological complex relaxation phenomena. Finally, a unified approach is briefly discussed that, in principle, allows combining both the long time (discrete) and short time (continuous) descriptions of relaxation behaviors for polymers in the rubbery and glassy regions.

Keywords: Non-equilibrium thermodynamics, Viscoelasticity, Free energy, Dissipation, Strain, Stress

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¹ Corresponding author, e-mail: leonov@uakron.edu

1. Introduction

The general mathematical structure of the linear theory of viscoelasticity has been established almost fifty years ago by Gross (1953), with more details elaborated by Bland (1960). In accordance with these texts, modeling solid-like linear viscoelasticity should include a linear hereditary functional with a convex kernel representing the relaxation function, and an out-of-integral linear elastic term that models the equilibrium elastic effects. In another approach, Meixner (1953,1954) and Biot(1955) developed the theory of linear viscoelasticity on the basis of non-equilibrium thermodynamics, whose general theoretical framework was established later by de Groot and Mazur(1962). Numerous applications of linear viscoelasticity to characterization and analyses of viscoelastic properties of liquid and solid polymers were considered in the text by Ferry (1980). If the volume (bulk) deformations are also important in linear region, the linear viscoelastic description should generally include two viscoelastic spectra, one for shearing and another for bulk viscoelasticity. Leonov (1996) recently discussed the non-equilibrium thermodynamic approach to non-isothermal bulk relaxations. It is well known Ferry, (1980) that the bulk relaxations are usually much faster than the shearing ones. Therefore except studying solely bulk relaxations, when both the shear and bulk relaxations proceed together, the effects of volume relaxations can be ignored.

The big obstacle in constructing a uniform thermo-mechanical description of polymers is their “thermo-rheological complexity”, well documented during the last decade in many papers by Plazek, Ngai, Roland and coworkers (e.g. see: Plazek et al, 1992; Ngai et al, 1997; and Roland et al, 1997). In these papers, different temperature dependences for different parts of relaxation spectra were observed over a very broad region of relaxation times or frequencies that includes all the basic types (flow, rubbery and glassy) of polymer mechanical behavior.

In the flow and rubbery regions, the uniform Williams-Landell-Ferry (WLF) time-temperature scaling (e.g. see Ferry, 1980) is valid for relaxation parameters describing different relaxation modes. This scaling uses the concept of entropy elasticity (e.g. see Treloar, 1975), where the equilibrium elastic modulus is proportional to the absolute temperature, and the same temperature dependencies apply for modal viscosities and elastic module. In these regions, the relaxation spectra for many polymers are well described by the Prony series with a relatively small number of relaxation modes. However, in the glassy region where the fractal properties of polymers dominate, another time-temperature scaling exists. The viscoelastic effects in this region are well described by a continuous distribution of relaxation spectrum, such as the stretching exponent and/or fractional derivative approaches (e.g. see Schiessel et al, 2000). Employing the Prony series in this region, though possible, is impractical since the discrete relaxation spectrum, being densely populated, would include numerous discrete relaxation modes.

It has been demonstrated that a possibility to describe the thermo-rheological complexity is by matching both the time-temperature scales when using a conceptual, semi-empirical, “mode coupling” model (e.g. see Ngai et al, 1997). This model sometime uses more than two matching procedures, when additionally the Rouse relaxation region (e.g. see Ferry, 1980) is involved. Some additional arguments have been applied within context of this model to cross-linked rubbers (Roland et al, 1997).

Several molecular-based theoretical approaches to linear relaxation phenomena in cross-linked rubbers have also been recently developed (Vigilis and Heinrich, 1994; Bastide and Boue, 1996; Gotlib and Gurtovenko, 1997). In these theories, a rubber has been modeled as “molecular network” filled with a Newtonian liquid, with the polymer chains in network being modeled as in the classic statistical theory of rubber elasticity. The interactions between the liquid and network and between the segments of the same strands were modeled as different types of viscous friction. These approaches are aimed at a theoretical derivation of discrete relaxation spectra with only a few physical parameters. Whereas Gotlib and Gurtovenko (1997) analyzed the homogeneous polymer network with a “classical” elastic contribution, Bastide and Boue (1996) studied the effect of topology on the network elasticity, and Vigilis and Heinrich (1994) analyzed the effects of the network heterogeneity, such as different types of disorder in the network structure and topology.

Some efforts were also made to develop mathematical procedures for finding the relaxation spectra directly from experimental data, which has long been established as generally an ill-posed problem (e.g. see review in paper by Simhambhatla and Leonov, 1993). Several regularization methods with the use of computerized procedures have been developed in the literature to overcome this difficulty. Nonetheless, these procedures of extracting the Prony parameters still depend highly on initial guesses about the numbers of relaxation modes, and usually operate with very high numbers of these. Fulcheron et al (1993) and Simhambhatla and Leonov (1993) demonstrated that the Pade-Laplace method is a more reliable tool for experimental determination of relaxation spectra when represented by a Prony series. It operates with an analytical continuation of the relaxation function into the complex plane where the problem of extraction of relaxation spectra is well posed and describes the Prony series with considerable less numbers of relaxation modes. A computerized Pade-Laplace procedure for extracting relaxation modes from a combination of different experiments was developed and demonstrated in a paper by Simhambhatla and Leonov (1993) and in the Ph.D. thesis by Simhambhatla (1994). In practical applications of the procedure to a viscoelastic solid, the true elastic (out-of-integral) component should be found first and then excluded from the Pade-Laplace procedure. The same is true for the cross-linked polymers or elastomers. No quantitative application of such an approach to solid-like viscoelasticity has yet been demonstrated.

The structure of the present paper is as follows. We first consider the general thermodynamic scheme for analyzing the solid-like viscoelastic phenomena, much similar to that published earlier in papers by Meixner (1953,1954), Biot (1955) and Leonov (1996). Then at the end of the paper we discuss the extension of our scheme to incorporate the effects of thermo-rheological complexity. We analyze in this paper only incompressible (shearing) solid like relaxations. This is because out of two (bulk and shearing) independent, linear relaxation phenomena, the non-isothermal bulk relaxations have been recently discussed by Leonov (1996).

2. State Variables and Free Energy Function

We hypothesize that the complete set of macroscopic state variables, sufficient to describe the linear shearing viscoelasticity are: the temperature T , the actual (total)

infinitesimal, traceless Hencky strain tensor \underline{h}_0 , and the set of “hidden” tensor variables $\{\underline{h}_k\}$ ($k=1,2,\dots,n$), depending generally on the space-time variables \underline{x}, t . Although a linear theory does not necessitate knowing the physical sense of the hidden variables \underline{h}_k , we can guess, and justify later, that they represent elastic strain contributions in the total viscoelastic strain originated from k -th physical mechanisms. Due to this guess we assume that the tensors \underline{h}_k are traceless, symmetric, second-order tensors. We also assume that the hidden variables \underline{h}_k , describing pure non-equilibrium properties of the system, vanish in the equilibrium.

We now introduce the specific (per mass unit) Helmholtz’ free energy F depending on the above set of state variables:

$$F = F(T; \underline{h}_0, \underline{h}_1, \dots, \underline{h}_n) \quad (\text{tr} \underline{h}_0 = \text{tr} \underline{h}_k = 0). \quad (1)$$

The specific entropy, S , and all other specific potentials, such as internal energy U , can then be found using common thermodynamic formulas, including, the Gibbs’ relation:

$$dU = dF + TdS, \quad U = F + TS, \quad S = -\partial F / \partial T \Big|_{\underline{h}_0, \underline{h}_k}, \text{ etc.} \quad (2)$$

Near the equilibrium, unloading state, which is far away from possible phase transitions, the free energy F is represented as a quadratic, positively definite form:

$$\rho \Delta F \equiv W = 1/2 G_0(T) \text{tr} \underline{h}_0^2 + 1/2 \sum_{k,j=1}^n G_{kj}(T) \text{tr}(\underline{h}_k \cdot \underline{h}_j), \quad (3)$$

corresponding to the minimum of the free energy. Here W is called the elastic potential. The positive definiteness of form (3) means that the equilibrium shear modulus G_0 is positive and the $n \times n$ symmetric *energetic* matrix, $\|G_{kj}(T)\|$ is positive definite, too.

In thermodynamic equilibrium under a stress action,

$$\underline{\sigma}_0 = \partial F / \partial \underline{h}_0 \Big|_{\underline{h}_k=0} = G_0 \underline{h}_0, \quad \partial F / \partial \underline{h}_k \Big|_{\underline{h}_k=0} = 0. \quad (4)$$

Here $\underline{\sigma}_0$ is the equilibrium *extra-stress tensor*, i.e. stress without isotropic pressure. The second formula in (4) is a consequence of our assumption that the hidden variables \underline{h}_k vanish in equilibrium. Namely because of this, the possible interactive term

$$\sum_{k=1}^n M_k(T) \text{tr}(\underline{h}_0 \cdot \underline{h}_k) \text{ is absent in (3).}$$

3. Clausius-Duham Inequality and Non-Isothermal Relaxation Phenomena

To analyze the behavior of the system in non-equilibrium, the common expression for the entropy production (or source of entropy) P_S is employed in the form:

$$TP_S = -T^{-1} \underline{q} \cdot \underline{\nabla} T + \text{tr}(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - dW / dt \Big|_T \quad (\geq 0). \quad (5)$$

Here \underline{q} is the thermal flux, $\underline{\nabla}$ is the space gradient symbol, $\underline{\underline{e}}$ is the (traceless) strain rate tensor, and $\underline{\underline{\sigma}}$ is the extra stress tensor. The inequality in the bracket of (5) indicates that according to the second law, the entropy production P_S must be positive for all non-equilibrium processes and vanish in equilibrium. With this inequality, the right-hand side of (5) represents the well-known Clausius-Duham inequality.

Substituting (3) into (5) yields:

$$TP_S = -T^{-1} \underline{q} \cdot \underline{\nabla} T + \text{tr}(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - \sum_{k=0}^n \text{tr}(\underline{\underline{\sigma}}_k \cdot d\underline{\underline{h}}_k / dt) \quad (\geq 0), \quad (6)$$

where

$$\underline{\underline{\sigma}}_0 = G_0(T) \underline{\underline{h}}_0, \quad \underline{\underline{\sigma}}_k = \sum_{j=1}^n G_{kj}(T) \underline{\underline{h}}_j. \quad (7)$$

Instead of tensors $d\underline{\underline{h}}_k / dt$, we now formally introduce new kinematical variables, the second-order traceless tensors $\underline{\underline{e}}_k^p$, satisfying the “evolution equations”:

$$d\underline{\underline{h}}_k / dt + \underline{\underline{e}}_k^p = \underline{\underline{e}} \quad (k = 0, 1, 2, \dots, n). \quad (8)$$

Evidently $\underline{\underline{e}}_0^p = \underline{\underline{0}}$ for $k = 0$, since the well-known kinematical relation for $\underline{\underline{h}}_0$ is:

$$d\underline{\underline{h}}_0 / dt = \underline{\underline{e}}. \quad (9)$$

For $k \geq 1$, the unknown tensors $\underline{\underline{e}}_k^p$ in (8) characterize the irreversible effects, and in fact, the evolution equations (8) simply represent the definition of tensors $\underline{\underline{e}}_k^p$.

Substituting now (8) with account for (9) into (6) yields:

$$TP_S = -T^{-1} \underline{q} \cdot \underline{\nabla} T + \text{tr}[(\underline{\underline{\sigma}} - \underline{\underline{\sigma}}_T) \cdot \underline{\underline{e}}] + \sum_{k=1}^n \text{tr}(\underline{\underline{\sigma}}_k \cdot \underline{\underline{e}}_k^p) \quad (\geq 0), \quad \underline{\underline{\sigma}}_T = \sum_{k=0}^n \underline{\underline{\sigma}}_k. \quad (10)$$

Here $\underline{\underline{\sigma}}_T$ is called the thermodynamic (extra) stress tensor, since it is completely

determined by the free energy function W .

Equation (10) distinctly demonstrates three sources of dissipation in the system: (i) non-isothermality, (ii) the deviation of the actual stress $\underline{\underline{\sigma}}$ from the thermodynamic one $\underline{\underline{\sigma}}_T$, and (iii) non-equilibrium dissipative effects originated in the above n irreversible physical mechanisms. The last two terms in (10) are called the mechanical dissipation. The sense of the second source of irreversibility is easily demonstrated in the case when the irreversible contributions in viscoelasticity, the tensors $\underline{\underline{h}}_k$, vanish. Then $\underline{\underline{\sigma}}_T = \underline{\underline{\sigma}}_0$, and the second term in the first equation in (10) correspond to a dissipative mechanism of the Kelvin-Voigt type. This mechanism denies “instantaneous elasticity”, as observed in experimental studies. The existence of instantaneous elasticity necessitates $\underline{\underline{\sigma}}_T = \underline{\underline{\sigma}}_0$. Thus for a modeling of the observable viscoelasticity with instantaneous response, (10) takes the final form:

$$TP_S = -T^{-1} \underline{\underline{q}} \cdot \underline{\underline{\nabla}}T + \sum_{k=1}^n tr(\underline{\underline{\sigma}}_k \cdot \underline{\underline{e}}_k^p) \quad (\geq 0), \quad \underline{\underline{\sigma}} = \underline{\underline{\sigma}}_T = \sum_{k=0}^n \underline{\underline{\sigma}}_k. \quad (11)$$

The entropy production in (10) (as well as in (11)) is represented as a typical bilinear form of the type $\sum_m X_m \cdot Y_m$. The independent quantities $\underline{\underline{\nabla}}T$ and $\underline{\underline{\sigma}}_k$ in (11) are treated as the “thermodynamic forces”, X_m , and conjugated to them are the independent quantities, $\underline{\underline{q}}$ and $\underline{\underline{e}}_k^p$, known as the “thermodynamic fluxes”, Y_m . Note that the thermodynamic fluxes are represented via time derivatives that change their signs under the reverse time transformation, $t \rightarrow -t$. In the linear scheme of non-equilibrium thermodynamics, the independent thermodynamic forces and fluxes are related via linear phenomenological relations with temperature dependent scalar coefficients. These relations include, in particular, the constitutive equations for the relaxation phenomena. Although the general case (10) is easy to analyze, we consider below only more physically meaningful and simple case described by (11). Then the linear, phenomenological, constitutive relations take the form:

$$\underline{\underline{e}}_k^p = \sum_{m=1}^n A_{kj}(T) \underline{\underline{\sigma}}_j, \quad (12)$$

$$\underline{\underline{q}} = -\lambda(T) \underline{\underline{\nabla}}T. \quad (13)$$

Such basic principles as simple arguments of the tensor dimensionality (Curie’s principle) and Onsager’s principle of symmetry for kinetic coefficients A_{km} have been taken into account in the constitutive relations (12) and (13). Substituting these into (11) yields:

$$TP_S = T^{-1} \lambda |\underline{\underline{\nabla}}T|^2 + \sum_{k,j=1}^n A_{kj}(T) tr(\underline{\underline{\sigma}}_k \cdot \underline{\underline{\sigma}}_j) \quad (\geq 0) ; \quad \underline{\underline{\sigma}} = \underline{\underline{\sigma}}_T = \sum_{k=0}^n \underline{\underline{\sigma}}_k. \quad (14)$$

Here the second term in the right-hand side of the first relation in (14) represents the contribution in entropy production due to mechanical dissipation. According to the second law, the entropy production must be positive in non-equilibrium. Because the two terms in (14) are independent, the coefficient of heat conductivity, λ , is positive and the kinetic matrix $\|A_{kj}\|$ is positive definite, too.

Expressing e^p via $\underline{\sigma}$ due to (12), and in turn, $\underline{\sigma}$ via \underline{h} due to the second relation in (7), yields:

$$d\underline{h}_k / dt + \sum_{m,j=1}^n A_{km}(T)G_{mj}(T)\underline{h}_j = \underline{e} \equiv d\underline{h}_0 / dt; \quad \underline{\sigma} = G_0(T)\underline{h}_0 + \sum_{k,j=1}^n G_{kj}(T)\underline{h}_j \quad (15)$$

$$(k = 1, 2, \dots, n)$$

Equations (15) represent the general formulation of linear constitutive equations for viscoelastic solids with instantaneous elasticity. They also justify our previous guess that the hidden variable \underline{h}_k is elastic contribution from the k-th non-equilibrium physical mechanism.

4. Normal Relaxation Modes: Thermo-Rheological Simplicity

In order to demonstrate that the general, linear, solid, viscoelastic constitutive equations (15) reduce to the normal (or independent relaxation) modes, we initially employ the assumption of the thermo-rheological simplicity:

$$G_{kj}(T) = G_0(T)g_{kj}, \quad A_{kj}(T) = a_{kj} / \eta_0(T). \quad (16)$$

Here $G_0(T) (\sim T)$ is the shear modulus known in rubber elasticity (e.g. see Treloar, 1975), $\eta_0(T)$ is a characteristic viscosity that far away from the glass transition is described by the Arrhenius dependence; $\|g_{kj}\|$ and $\|a_{kj}\|$ are numerical $n \times n$, symmetric and positive definite matrices. The application of general scaling formulae (16) to polymeric materials has been widely discussed by Ferry (1980). Although the assumption of thermo-rheological simplicity has been criticized in cited papers by Plazek, Ngai, Roland et al, it still approximately holds for polymers above their glass transition temperature for restricted frequency and time intervals.

Because both the numerical $n \times n$ matrices, $\|g_{kj}\|$ and $\|a_{kj}\|$, are symmetric and positive definite, it is possible to introduce the “normal coordinates”, tensors $\hat{\underline{h}}_k(t, \underline{x})$, as follows:

$$\hat{\underline{h}}_k = \sum_{j=1}^n q_{kj} \underline{h}_j \quad (k = 1, 2, \dots, n). \quad (17)$$

Here $\|q_{ki}\|$ is a numerical orthogonal $n \times n$ matrix that reduces simultaneously both the matrices $\|g_{kj}\|$ and $\|a_{kj}\|$ to the diagonal form with respective principal values g_k and a_k . Under the transformation (17), the constitutive equations (15) take the form:

$$d\underline{\hat{h}}_k / dt + \underline{\hat{h}}_k / \theta_k(T) = \underline{e} = d\underline{h}_0 / dt; \quad \underline{\sigma} = G_0(T)\underline{h}_0 + \sum_{k=1}^n G_k(T)\underline{\hat{h}}_k \quad (k = 1, 2, \dots, n). \quad (18)$$

Here the parameters $G_k(T)$ and $\theta_k(T)$ are defined as follows:

$$G_k(T) = G_0(T)g_k; \quad \theta_k(T) = \frac{\theta_0(T)}{a_k g_k}, \quad \theta_0(T) \equiv \eta_0(T) / G_0(T). \quad (19)$$

Without loss of generality, we now assume that components of the numerical matrices $\|g_{kj}\|$ and $\|a_{kj}\|$ are sorted so that the products of their principal values, $g_k a_k$, monotonically decrease with increasing number k , i.e. downwards along the main diagonal. Therefore, due to (19),

$$a_k g_k \leq a_{k+1} g_{k+1}; \quad \theta_k(T) \geq \theta_{k+1}(T). \quad (20)$$

The choice of such a monotonous series is needed in the discrete case for formulating the common presentation of a relaxation spectrum, $G = G(\theta(T))_k$, with a possible formal continuous generalization. Evidently, the series $G_k(T)$ is generally non-monotonous.

The free energy function (3) and the contribution of mechanical dissipation in the entropy production (the second term in the first equation in (14)) can be expressed via the normal coordinates as follows:

$$W = 1/2 G_0(T) \text{tr}(\underline{h}_0^2) + 1/2 \sum_{k=1}^n G_k(T) \text{tr}(\underline{\hat{h}}_k^2), \quad (3a)$$

$$D = TP_S|_T = \sum_{k,j=1}^n [G_k(T) / \theta_k(T)] \text{tr}(\underline{\hat{h}}_k^2) \quad (\geq 0). \quad (14a)$$

Consider also the integral form of the above formulas in isothermal case when $G_k(T)$ and $\theta_k(T)$ are constant. Integrating the first equation in (18) and substituting the result in the second one, yields:

$$\underline{\hat{h}}_k(t) = \int_{-\infty}^t \exp[-(t-\tau) / \theta_k] d\underline{h}_0(\tau), \quad \underline{\sigma}(t) = G_0 \underline{h}_0(t) + \int_{-\infty}^t \psi(t-\tau) d\underline{h}_0(\tau) d\tau. \quad (21)$$

Here $\psi(t)$ is the relaxation function defined for the discrete relaxation spectrum $\{G_k, \theta_k\}$ as the Prony series:

$$\psi(t) = \sum_{k=1}^n G_k \exp(-t/\theta_k). \quad (22)$$

Formulae (3a) and (14a) can also be represented in the form:

$$W = 1/2 G_0(T) \text{tr}[\underline{h}_0^2(t)] + 1/2 \int_{-\infty}^t \int_{-\infty}^t \psi(2t - \tau_1 - \tau_2) \text{tr}[d\underline{h}_0(\tau_1) \cdot d\underline{h}_0(\tau_2)]. \quad (3b)$$

$$D = -1/2 \int_{-\infty}^t \int_{-\infty}^t \psi(2t - \tau_1 - \tau_2) \text{tr}[d\underline{h}_0(\tau_1) \cdot d\underline{h}_0(\tau_2)]. \quad (14b)$$

Here $\psi(2t - \tau_1 - \tau_2) \equiv d\psi(t)/dt|_{t \rightarrow 2t - \tau_1 - \tau_2} (\leq 0)$. Formulae (21), (22), (3b), and (14b) are well known in the linear viscoelasticity with a discrete relaxation spectrum (Gross, 1953; Bland, 1960).

In accordance with observations, the temperature variations of the elastic modulus G_0 in the non-isothermal case are usually neglected. Then the new time-like, non-dimensional variable t^* is introduced as follows:

$$t^* = \int_{-\infty}^t d\tau / \theta(T(\tau)). \quad (23)$$

Using the characteristic modulus $G_0(T)$ and relaxation time $\theta_0(T)$ as scaling parameters, it is possible to represent the constitutive equations (18) in non-dimensional, temperature independent form, which demonstrates the well-known time-temperature superposition principle. When it is applicable to experimental viscoelastic data, they are represented in the form of "master curves". The dependence $G_0(T)$ is commonly used in the form of that known in the rubber elasticity (Treloar, 1975), whether the solid-like or liquid-like viscoelasticity is studied. The dependence $\theta_0(T)$ above the glass transition temperature is commonly used in the WLF form, which at higher temperatures is reduced to the familiar Arrhenius form.

5. Normal Relaxation Modes: Thermo-Rheological Complexity

In this case both thermodynamic matrices, $\|G_{ik}\|$ and $\|A_{ik}\|$ can be transformed under isothermal conditions to the diagonal form, i.e. the isothermal problem once again can be reduced to the analysis of independent, normal relaxation modes. However, the factorization (16) is not valid here anymore. It means that there is a dependence of the temperature parameters on the number of the discrete relaxation mode. In other words, different temperature dependences exist in this case in various parts of relaxation spectrum. Luckily, the experimental observations by Plazek, Ngai, Roland and their coworkers, cited above, found these temperature dependencies to be relatively simple,

with mostly two consequent intervals of the relaxation spectrum having different temperature scales. According to the thermodynamic approach demonstrated in this paper, it means that there are negligible physical interactions between these almost independent parts of the relaxation spectrum.

This situation found a sound physical interpretation, especially in the case of polymer melts with very long and flexible polymer chains and narrowly distributed molecular weight (e.g. see Ngai et al, 1997). It has been revealed that for these polymers, three different relaxation spectra can be introduced that relate to the three different scales of molecular motion. These are: (i) the supra-molecular scale where motions of large entangled macromolecules, which being almost independent on the intra-molecular chemical chain structure, contribute to the dynamic module in the flow and plateau regions; (ii) the intermediate, Rouse's molecular scale of motion, which is independent of the presence of entanglements, and being nearly independent of intra-molecular chemical chain structure, contributes to the ascending (after plateau) region in the dynamic module; and (iii) the glassy region with a small intra-molecular scale of motion, which depends highly on the chemical structure of monomer units in polymer chains. Remarkably, the molecular motions within these three scales can be considered as practically independent. Almost the same physical picture can be found in (usually slightly) cross-linked rubbery materials (Roland et al, 1997), except for the first large-scale molecular motion region, which is now mostly affected by the cross-links. This is the case considered in the present paper.

In our opinion, the intermediate, Rouse's temperature scaling should have the same WLF temperature dependence of typical relaxation phenomena, as the first large scale motions of polymer chains. This scaling has been introduced by Ngai et al (1997) to narrow the "disagreement band" and obtain perfectly smooth master curves. Since the temperature scaling is in principle different only in two regions, glassy and flow/rubbery, we develop below an example using a two-scale approach. However, there is no difficulty to extend it for as many temperature dependences as needed.

In order to describe this complex thermo-rheological behavior, we make a simplifying assumption that the above two molecular motions are completely independent. In our formal scheme it may happen only if both the energetic, $\mathbf{G}_n = \|\|G_{ik}\|\|$, and kinetic, $\mathbf{A}_n = \|\|A_{ik}\|\|$, $n \times n$ matrices have similar diagonal block structures (see Appendix). It means that the suggested structure of these matrices is that of similar diagonal block matrices (DB) matrices that represent the above two main molecular mechanisms of polymer motions as:

$$\mathbf{G}_n = \text{diag}\{\mathbf{G}_{r_1}, \mathbf{G}_{r_2}\}, \mathbf{A}_n = \text{diag}\{\mathbf{A}_{r_1}, \mathbf{A}_{r_2}\}, \mathbf{G}_n \sim \mathbf{A}_n \quad (r_1 + r_2 = n) \quad (24)$$

The corresponding rank of r_k component matrices \mathbf{G}_{r_k} and \mathbf{A}_{r_k} in Eq.(24) are symmetric, positive definite, and are assumed to be represented in the partially factorized form:

$$\mathbf{G}_{r_k} = G_k(T)\mathbf{g}_{r_k}, \mathbf{A}_{r_k} = \eta_k(T)\mathbf{a}_{r_k} \quad (k=1,2); G_0(T)/G_1(T) = c = \text{const.} \quad (25)$$

Here \mathbf{g}_{r_k} and \mathbf{a}_{r_k} ($k = 1,2$) are symmetric and positive definite numerical rank of

r_k matrices.

We now use the orthogonal DBM, $\mathbf{Q}_n = \text{diag}\{\mathbf{Q}_{r_1}, \mathbf{Q}_{r_2}\}$, ($r_1 + r_2 = n$) that consists of orthogonal rank r_i numerical matrices \mathbf{Q}_{r_i} of the same structure as shown in Eqs.(24) and (25), and reduce the DB matrices \mathbf{G}_n and \mathbf{A}_n to the diagonal form:

$$\begin{aligned} \mathbf{G}_n^* &= \mathbf{Q}_n \cdot \mathbf{G}_n \cdot \mathbf{Q}_n^T = \text{diag}\{G_i(T)\mathbf{Q}_{r_i} \cdot \mathbf{g}_{r_i} \cdot \mathbf{Q}_{r_i}^T\} \Big|_{\sum_i r_i = n} \\ &= \text{diag}\{G_i(T)\text{diag}\{\mathbf{g}_k\}_{r_i}\} \Big|_{\sum_i r_i = n} \equiv \text{diag}\{G_k(T)\}_{k=1,2,\dots,n} \end{aligned} \quad (26)$$

$$\begin{aligned} \mathbf{A}_n^* &= \mathbf{Q}_n \cdot \mathbf{A}_n \cdot \mathbf{Q}_n^T = \{\eta_i(T)\mathbf{Q}_{r_i} \cdot \mathbf{a}_{r_i} \cdot \mathbf{Q}_{r_i}^T\} \Big|_{\sum_i r_i = n} \\ &= \text{diag}\{\eta_i(T)\text{diag}\{\mathbf{a}_k\}_{r_i}\} \Big|_{\sum_i r_i = n} \equiv \text{diag}\{A_k(T)\}_{k=1,2,\dots,n} \end{aligned}$$

It is also possible to introduce normal tensor coordinates, $\hat{h}_{\underline{k}}(t, \underline{x})$, as

$$\hat{h}_{\underline{k}} = \|\mathbf{Q}_n\|_{kj} h_{\underline{j}} \quad (27)$$

that reduce CE's (15) to the form of independent normal modes:

$$d\hat{h}_{\underline{k}}/dt + \hat{h}_{\underline{k}}/\theta_k^i(T) = \underline{e} = d\underline{h}_0/dt; \quad \underline{\sigma} = G_0(T)\underline{h}_0 + \sum_{i=1}^2 \sum_{k=r_i}^{r_i+1} G_k^i(T)\hat{h}_{\underline{k}}; \quad \sum_{i=1}^2 r_i = n. \quad (28)$$

Here the parameters $G_k^i(T)$ and $\theta_k^i(T)$ are defined as follows:

$$G_k^i(T) = G_i(T)g_k; \quad \theta_k^i(T) = \frac{\theta_i(T)}{a_k g_k} = \frac{\eta_i / G_i}{a_k g_k}, \quad (29)$$

where

$$\begin{aligned} G_i &= G_1, \quad 1 \leq k \leq r_1; \quad G_i = G_2, \quad r_1 \leq k \leq r_2; \\ \theta_i &= \theta_1, \quad 1 \leq k \leq r_1; \quad \theta_i = \theta_2, \quad r_1 \leq k \leq r_2; \end{aligned} \quad (30)$$

We assume without loss of generality once again that inequalities (20) hold. Therefore, one can construct the discrete relaxation spectrum $G = G(\theta(T))_k$, with an easy formal generalization for the continuous relaxation spectrum. Also, in the isothermal case, the formulae (21), (22) and also (3a,b) and (14a,b) hold true, however, with such a modification that the two different parts of the relaxation spectrum (22) have different

temperature dependences. We now assume that

$$\theta_1(T) \gg \theta_2(T). \quad (31)$$

These inequalities have been observed in all types of polymers as well as in cross-linked rubbers. Then inequalities (20) and (31) guarantee the partial scaling for dynamic and relaxation experimental data.

Consider as an example an interpretation of isothermal dynamic experiments, where harmonic oscillations with frequency ω are applied to a sample of a cross-linked rubber in a very wide range of frequencies and temperature. This is the situation where the thermo-rheological complexity cannot be ignored. The expressions for the real $G'(\omega)$ and imaginary $G''(\omega)$ parts of the complex dynamic module are:

$$G'(\omega) = G_0 + G_1 \sum_{k=1}^{r_1} g_k \frac{(\omega\theta_1 g_k a_k)^2}{1 + (\omega\theta_1 g_k a_k)^2} + G_2 \sum_{k=r_1+1}^{r_2} g_k \frac{(\omega\theta_2 g_k a_k)^2}{1 + (\omega\theta_2 g_k a_k)^2}; \quad (32)$$

$$G''(\omega) = G_1 \sum_{k=1}^{r_1} g_k \frac{\omega\theta_1 g_k a_k}{1 + (\omega\theta_1 g_k a_k)^2} + G_2 \sum_{k=r_1+1}^{r_2} g_k \frac{\omega\theta_2 g_k a_k}{1 + (\omega\theta_2 g_k a_k)^2}.$$

Using the inequalities (20) and (31), one can show that there are two different consecutive “temperature independent” scaling for both $G'(\omega)$ and $G''(\omega)$ in their corresponding parts of the frequency range:

$$\frac{G'(\omega\theta_1(T))}{G_1(T)}, \quad \frac{G''(\omega\theta_1(T))}{G_1(T)} : 0 < \omega\theta_1 \ll 1/(g_{r_1} a_{r_1}) \quad (33)$$

$$\frac{G'(\omega\theta_2(T))}{G_2(T)}, \quad \frac{G''(\omega\theta_2(T))}{G_2(T)} : 1/(g_{r_1} a_{r_1}) < \omega\theta_2 \ll 1/(g_{r_2} a_{r_2}).$$

Similar types of scaling can be employed to other viscoelastic tests, such as creep or relaxation after suddenly applied constant strain, *etc.* It should be noted that applicability of the proposed scaling to creep data is based on the well-known fact that for the discrete viscoelastic spectra, the retardation spectrum is “imbedded” into the relaxation one, so $\theta_k > \bar{\theta}_k > \theta_{k+1}$ (e.g. see Bland, 1960). Here $\bar{\theta}_k$ are points belonging to retardation spectrum. It means that in continuous approximations of the viscoelastic spectra, both spectral regions coincide.

As mentioned, the continuous relaxation spectra are commonly employed in the description of relaxation phenomena in the glassy state. This means that the above thermodynamic scheme, which uses a discretized matrix approach with densely populated interactive matrices for the fast relaxation phenomena, should be changed to a continuous, integral approach. Although this change is quite physically transparent, its formal, strict development is still desired. As established here a unified scheme can

combine both the long time (discrete) and short time (continuous, or densely populated discretized) approaches to relaxations of polymers in rubbery and glassy regions.

6. Conclusion

The thermodynamic derivation of linear viscoelastic constitutive equations discussed above can be seen as a justification for the completely phenomenological theory of linear viscoelasticity. In the thermo-rheological simple case, we used the time-temperature superposition principle to reduce the constitutive equations to the form of normal (non-interactive) relaxation modes. This derivation is quite similar to the well-known derivations from the papers by Meixner (1953,1954) and Biot (1955) (see also Leonov, 1996). The thermodynamic derivation of linear viscoelastic constitutive equations in the thermo-rheological complex case assumes different types of independent equilibria and non-equilibrium interactions between the various polymeric subsystems. We have modeled these independent interactions using a well-known formalism of diagonal block matrices. This approach can also be applied to model dielectric relaxations for thermo-electrically complex cases.

The demonstrated theory creates a solid thermodynamic framework for the more detailed, molecular models. These present valuable and complementary parts to continuum approaches because they can answer the important unresolved questions about the size and “density” of population of interactive elements, along with different temperature dependencies of the independent interactions. For example, if the density of interactive elements of microstructure is high, as usually happens in the glassy region, then enormous amounts of interactive elements should be involved in the rapid relaxation response. These rapid relaxations can be successfully described by various continuous approaches, such as the “stretched exponential” and fractional calculus approaches (Schiessel et al, 2000), related to the fractal physics of these relaxation phenomena. Although in this paper we demonstrated the thermodynamic approach as applied to discretized relaxation phenomena, the approach could be easily extended to the continuous case, when operating with integral equations, instead of matrices.

The thermodynamic framework for linear viscoelasticity in both thermo-rheological simple and complex cases can also be used by applying such a direct and mathematically well-posed procedure as developed by the Pade-Laplace method applied to viscoelastic phenomena by Fulcheron et al (1993) and Simhambhatla and Leonov (1993) for finding the effectively discretized relaxation spectrum directly from experimental data. This method can also be applied to different parts of the relaxation spectrum under various constant temperatures to reveal their possible different temperature dependencies. It is of interest to use the Pade-Laplace method for effective discretization of continuous relaxation spectra, such as stretched exponential or the Mittag-Leffler function,, to evaluate the density of population for the various relaxation mechanisms.

In the case of rubber viscoelasticity, it is also of interest to find the change in relaxation spectrum and its temperature dependence during the cure reaction when the emerging cross-links change the rubber state from flowing (“green”) to completely cured cross-linked rubber. Such an approach has been initiated by Mitra (2000) to reveal the change in the linear viscoelastic spectrum during the cure reaction, however, without

application of the Pade-Laplace technique.

Appendix 1: Diagonal Block Matrices

Let \mathbf{M}_n be a $n \times n$ matrix and $\{\mathbf{M}_r\}$ ($r < n$) be a set of $r \times r$ matrices. We define the diagonal block (DB) matrix as a combined \mathbf{M}_n matrix representing a diagonal, ordered sequence of the component matrices \mathbf{M}_r :

$$\mathbf{M}_n = \text{diag}\{\mathbf{M}_{r_1}, \mathbf{M}_{r_2}, \dots, \mathbf{M}_{r_k}\} = \begin{pmatrix} \mathbf{M}_{r_1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{M}_{r_2} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \cdot & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{M}_{r_k} \end{pmatrix} \quad \sum_k r_k = n. \quad (\text{A1})$$

Obviously, the order in the diagonal sequence (A1) is essential.

Consider now the case when the component matrices \mathbf{M}_r are symmetric and positive definite. Then it is evident that for any combination in Eq.(A1), the DB matrix \mathbf{M}_n is symmetric and positive definite. We call the component matrices properly sorted if their principle values increase along the diagonal downwards. A DB matrix is called monotonous if the combined principal values of its properly sorted component matrices monotonically increase or decrease along the diagonal downwards. The structure of a DBmatrix is defined by the consequence of the component matrices of various (in particular, the same) allowed ranks. Two DB matrices are called similar if their component matrices are of the same structure and have the same properties, i.e. if they are, e.g., symmetric or positive definite, or orthogonal, etc.

Consider now a vector $X_n \in \mathfrak{R}_n$ and a linear operation in \mathfrak{R}_n , represented by a DB matrix, \mathbf{M}_n :

$$Y_n = \mathbf{M}_n \cdot X_n = \sum_i \mathbf{M}_{r_i} \cdot X_{r_i} = \sum_i Y_i, \quad Y_i \in \mathfrak{R}_{r_i}, \quad \sum_i r_i = n. \quad (\text{A2})$$

Equation (A2) demonstrates that any $n \times n$ DB matrix \mathbf{M}_n with a given structure fractions the total space \mathfrak{R}_n into the full set of mutually orthogonal, non-intersecting subspaces \mathfrak{R}_{r_i} of lesser dimensionality. Equation (A2) holds for any DB matrix of various structures. For example, if the \mathbf{M}_{r_i} in (A2) are orthogonal, i.e. $\mathbf{M}_{r_i} = \mathbf{Q}_{r_i}$, the transformation (A.2) is orthogonal. If the \mathbf{M}_{r_i} are symmetric $r_i \times r_i$ component matrices in a DB matrix, with principal values m_{r_i} , and \mathbf{Q}_{r_i} are the $r_i \times r_i$ component matrices of the orthogonal DB matrix, which reduce the component matrices \mathbf{M}_{r_i} to the diagonal form, \mathbf{M}_n^* , then

$$\mathbf{M}_n^* = \mathbf{Q}_n \cdot \mathbf{M}_n \cdot \mathbf{Q}_n^T = \sum_i \text{diag}\{\mathbf{Q}_i \cdot \mathbf{M}_i \cdot \mathbf{Q}_i^T\} \Big|_{\sum_i \tau_i = n} = \text{diag}\{m_k\}_{k=1,2,\dots,n} \quad (\text{A.3})$$

The demonstrated above properties of DB matrices show that they behave quite similarly to regular diagonal matrices.

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